연료전지용 MXenes의 등장

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Emergence of MXenes for Fuel Cell

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Abstract

Recently, 2D materials greatly impact in the various applications especially in the energy conversion and storage devices. Among the 2D materials, nowadays researchers are showing their propensity towards the MXenes due to their potential structural and physical properties as well as their use in various applications. Recently, MXenes have been used as filler in polymer electrolytes membranes and as catalytic support to increase the performance of fuel cells (FCs). But this review covers only recent progress and application of MXenes in proton and anion exchange membranes for FCs. Also, this review will provide a significant guidance and broad overview for future research in MXenes based polymer electrolyte membrane for FCs.

Keywords: MXenes, Proton exchange membrane, Anion exchange membrane, Fuel cell

1. Introduction

Currently, fossil fuels are prime sources of energy to meet our daily needs. However, these energy sources are very limited and present exhaustion rate is very high due the high energy requirement for industrialization and development. Therefore, in near future these resources may be limited or disappeared. Also, these fuels are associated with lots of serious health and environmental hazardous. Therefore, entire world is looking for an alternative, cheaper and easy access green energy sources. Presently, solar energy, wind energy, hydro energy, tidal energy, geothermal energy, and biomass energy are the major sources of green energies. Although, these are best and cheap sources of energy, but many problems are associated with these, such as lack of energy storage systems, lack of continuous source for energy generation, requirement of land, infrastructure, political challenges, economic and financial challenges[1]. Therefore, peoples are looking for the other alternative energy sources that has potential to meet the pres-

ent energy demand. For this, fuel cell (FC) is prime and attractive electrochemical device that has the potential to meet the present and future energy demands. Apart from its potential, it has many advantages over the other comparable energy resources such as low-to-zero emissions, high efficiency, reliability, fuel flexibility, energy security, durability, scalability, and quiet operational process.

In FC, instead of the combustion process, electrochemical reactions occur at the anode and cathode to produce energy[2]. Hydrogen and oxygen are mixed in a FC to produce electricity, heat, and water. Today, a variety of vehicles, including cars, buses, trucks, forklifts, trains, and more, are moved using FC. FC is also used to power homes and businesses and to keep vital infrastructure, including hospitals, supermarkets, data centres, and operational.

FC is made of anode, cathode, and an electrolyte membrane. In a conventional FC, oxygen and hydrogen are passed through the cathode and anode, respectively. A catalyst at the anode site breaks the hydrogen molecules into protons and electrons. The electrons are pushed through a circuit and produce an electric current and extra heat, while the protons pass through the porous electrolyte membrane. Protons, electrons, and oxygen mix at the cathode to form water molecules. FCs are basically divided as according to their operations, electrolyte type and others[3,4]. These are direct methanol fuel cell (DEMFC), reversible fuel cell (RFC), alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC), anion exchange fuel cell (AEMFC), phos-

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phoric fuel cell (PFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC)[5].

In these FCs, membrane electrode assembly (MEA) is the heart which consist of anode, cathode, and an electrolyte membrane. As a result, this assembly provides the reaction cites for oxidation and reduction reactions as well as transmission channels for cation, anion, electron, gas, and water. Nowadays, polymer electrolyte membrane is the focused researched area in FCs because of their advantages. Therefore, the choice of materials in fabrication of polymer electrolytes membrane for cation and anion exchange is more prominent which are define the performance of the FCs. In the past, many materials have been used as additives or filler (carbon nanomaterials and metal oxide nanoparticles) fabrication of high performance ion (cation or anion) exchange polymer electrolyte membranes for FC[6].

Polymer electrolyte membranes for exchange of cation (proton) and anion (hydroxide) are play the significant role in the performance of respective FCs in which they have being used. These membranes should have high ionic conductivity, chemical stability, mechanical stability, and thermal stability as well as having the good gas and electronic insulating behaviour[7,8]. In this area, various perfluorinated and non-perfluorinated polymers have been used to fabrication of ion exchange membrane for FCs[9,10]. Particularly, polymers incorporated with cationic groups (ammonium and phosphonium etc) used for anion exchange membrane (AEM) and with anionic group (-SO$_3$H) used for proton exchange membrane (PEM). Apart from this, many fillers such as metal oxide nanoparticles and carbon nanomaterials etc. have been used in these polymers matrix to increase the performance and stability of ion exchange membrane[13-15]. In recent years, lots of research have been performed in these areas but still far from the easily accessible practical applications.

Recently, 2D materials such as graphene has shown great interest in FCs application as filler for polymer electrolyte membrane. However, graphene has the tendency of quick agglomeration in polymer matrix which reduced the performance of the final composites. Although, graphene oxide is the good alternative of graphene which showed the higher dispersion in polymer with or with functionalization but is has the lower structural and physical properties than the graphene. Therefore, recently a another 2D material, MXenes have shown potential to replace the graphene due to their high electronic conductivity, mechanical and chemical stability as well as provide ease of surface modification[16,17]. Due to their charming properties, they have been used in many applications such as batteries, supercapacitor, biomedical, and FCs etc[18-22].

MXenes are 2D layered inorganic materials which discovered in 2011 by Naguib et al.[23] from Drexel University, USA. The MXenes are generally having formula of $M_{n+1}X_nT_x$, where M is the early transition metals (Ti, V, Cr, Nb, etc), X is carbides (C), nitrides (N), or carbonitrides (CN) and T is representing the surface functionalities such as O, F, OH, H$_2$O, and/or Cl[24,25](Figure 1 (a)).The thickness and planer size of MXenes in several atoms and several micrometres [26,27]. MXenes having many charming properties such as large surface area, high mechanical, physicochemical and electronic properties
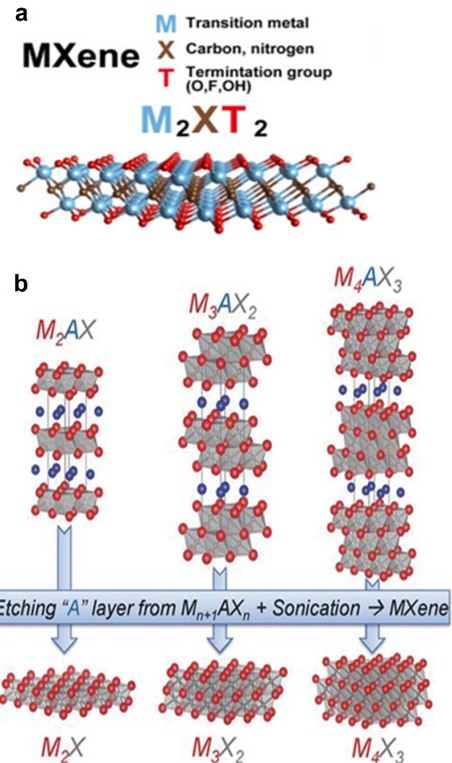

Figure 1. (a) MXenes (Reprint with the permission of Elsevier)[25], (b) MAX phases (Reprint with the permission of John Wiley and Sons)[31].
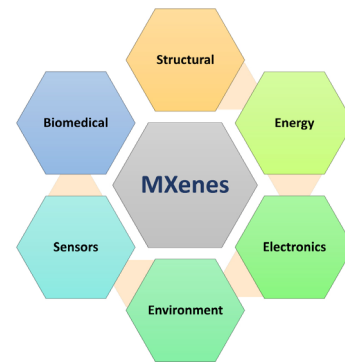

Figure 2. Application of MXenes.

as well as show excellent biocompatibility due to its unique structure [28]. In addition, metallic conductivity of MXenes is very high up to 15100 S/cm, modulus elasticity of 330~400 GPa and high optical transparency in Ti$_3$C$_2$T$_x$ film[29,30]. Due these properties, MXenes are extensively used in various applications such as catalyst, biomedical, polymer composites, electronics, environment, and energy (solar cell, batteries, supercapacitor, and FC) etc. (Figure 2). MXenes are generally prepared from chemical etching of MAX phase. MAX having general formula of $M_{n+1}AX_n$, where n=1, 2, or 3, M is an early transition metals, A is group 13 and 14 elements (Al, Si, Ga, In, and S) and X is C/N or both (Figure 1 (b)).

The MAX are hexagonal layered structure which distorted XM$_6$ oc-

tahedral interleaved by single layer of group 13 and 14 elements and X atoms are filling octahedra sites. Generally, three types of MAX phases such as M_2AX, M_3AX_2, and M_4AX_3 are known which have been used for the synthesis of MXenes[31](Figure 1 (b)).As according to these MAX phases different types of MXenes could be prepared by various methods. Presently, more than 60 MAX phases are known[32]. Recently, MXenes and MXenes based materials have been used in the development for polymer electrolyte membranes for FCs applications. Therefore, this review focused on the recent progress of MXenes based polymer electrolyte membranes for PEMFCs and AEMFCs.

2. Application of MXenes and MXenes based materials for PEM and AEM

2.1. Proton exchange membrane (PEM)

In PEMFCs, PEMs is the essential part of MEA that has ability to conduct proton in moist state. These PEMs are generally made of solid polymer electrolyte which has negatively charge species such as SO_{3-}, $-COO^-$, $-PO_3^{2-}$, $-PO_3H^-$, and $-C_6H_4O^-$, etc., for conducting proton [33,34]. For PEMs, Nafion® is frequently used as electrolyte membrane in PEMFCs because of its elevated proton conductivity, thermal stability, mechanical strength, chemical stability, and durability in the hydrated state[35]. Nafion® has many limitations such as high cost as well as presence of highly toxic fluorine which restricts its frequent use in industrial applications. Therefore, many non-fluorinated polymers such as poly (arylene ether) poly(arylene ether ether ketone) (PEEK), poly(arylene ether sulfone) (PES), polysulfone (PS), poly(imide) (PI), polybenzimidazole (PBI) and their derivatives with including high thermal and mechanical stability, oxidation resistance, and simple functionalisation with low cost have been investigated[36, 37]. These polymers-based membrane generally suffer excessive swelling as a results low mechanical strength and durability occurs, due to the presence of danse ionic groups[38]. To overcome this situation,many organic-inorganic heterostructure composite membranes have been used.In this composite, organic part provides processability, film forming properties, mechanical stability, and ion conductivity, on the other hand, inorganic part provides thermal and chemical stability

as well as reduced fuel crossover[39,40]. For inorganic part, many materials such as metal oxides, zirconia phosphate, boron phosphate, heteropoly acids, carbon nanomaterials and MXenes have been used as fillers in the organic part which increases the overall performance of the membranes[41-48]. Among these, MXenes gain tremendous attentions as a filler due to its high structure and physical properties for PEM to increase its overall performance.

Generally, hydroxyl (•OH), hydrogen (•H), and hydroperoxyl (•OOH) radical are formed with strong oxidative characteristics during FC operation[49-51]. These radicals are formed due to the incomplete ORR and responsible for the cleavage of unstable $-COOH$ terminal groups, the operational $-SO_3H$ group, and the ether linkages, resulting in the deprivation of membranes[49,52-54]. To overcome this problem, Zhao et al.[55] prepared the MXene$-CeO_2$ hybrid which helps to provide the resistance against the free radicals. They have prepared this hybrid by using hydrothermal process where appropriate amount of $Ce(NO_3)_3 \cdot 6H_2O$ in H_2O was added into $Ti_3C_2T_x$ MXene supernatant in the presence of NaOH base and reaction processed at 180 °C for 12 h (Figure 3). Finally, they obtained product after washed and freeze-dried for 24 h. Further, this hybrid dispersed in Triton X-100 and spray coated over the PTFE-reinforced proton exchange membranes (r-PEM). The hybrid membrane with loading of 0.1 mg/cm^2MXene$-CeO_2$ exhibited a low OCV decay rate (0.53 mV/h), hydrogen crossover of 2.6 mA/cm^2 and higher maximum power density (1222.5 mW/cm^2) than pristine r-PEM after accelerated degradation testing for 150 h. This effect arose due to the resistance exhibited by prepared hybrid towards the free radical formed during the FC operation.

Al-Othman et al.[56] studied MXenes incorporated zirconium phosphate (ZrP) filler for polytetrafluoroethylene (PTFE) with structure directing agents such as an ionic liquid (IL) and polyethylene glycol (PEG). The proton conductivities of prepared composites membrane are 0.006 S/cm and 0.05 S/cm for ZrP/MXene/PEG and PTFE/MXene/PEG/IL, respectively, that indicated the utility of incorporation of MXene in ZrP.Sulphonated-MXene ($Ti_3C_2T_x$-SO_3H) as filler was prepared for acidic sulfonated poly (ether ether ketone) (SPEEK) and basic chitosan (CS) polymer matrixes[57]. $T_3C_2T_x$-SO_3H
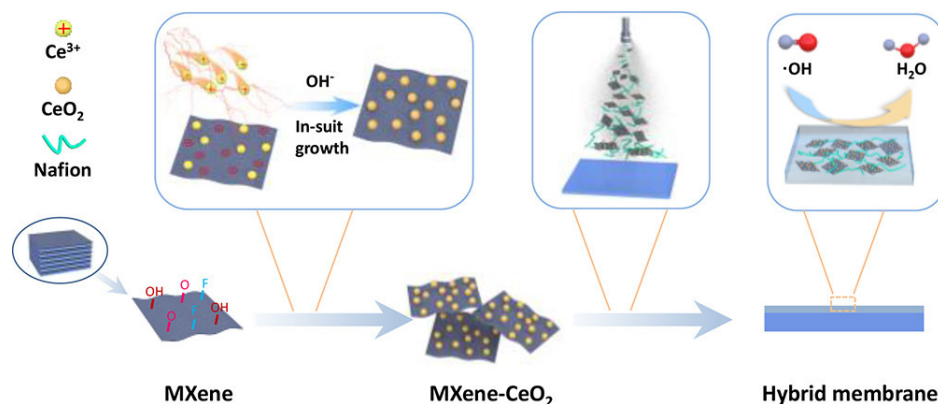

Figure 3. The procedure for synthesis a hybrid membrane with MXene$-CeO_2$ coating (Reprint with the permission of American Chemical Society)[55].

filler developed the conductive channel in polymer matrix which increases the proton conductive of fabricated membranes. Specifically, 10wt% of $Ti_3C_2T_x$-SO_3H increases proton conductivity of 144% and 66% for SPEEK and CS polymers, respectively, in hydrated condition. This MXenes based filler also increases thermal and mechanical stability of membranes. Particularly, 5 wt% of $Ti_3C_2T_x$-SO_3H in SPEEK exhibited tensile strength and Young modulus of 45.9 and 1010.9 MPa, respectively, which were higher than the tensile strength and Young modulus of pure SPEEK of 38.7 and 873.2 MPa, respectively.

Liu *et al.*[58] reported the effect of proton conductive properties of polymer by incorporation of $T_3C_2T_x$. They have prepared the Nafion or CS/$Ti_3C_2T_x$-X (in different weight percentage, X = 1, 2, 5, 10, or 20) composite through solution casting method. Incorporation of $Ti_3C_2T_x$ increases the thermal properties of Nafion and CS based membrane. Particularly, pure nafion membrane was showed the glass transition temperature (T_g) of 126 °C which was increased up to 127 and 132 °C after incorporation of $Ti_3C_2T_x$-2 and $Ti_3C_2T_x$-10, respectively (Figure 4 (a)). On the other hand, same trends were also found with the CS based membranes, transition temperature (T_d) of CS membrane was 219 °C which was increases up to 225, and 234 °C for CS/$Ti_3C_2T_x$-2, and CS/$Ti_3C_2T_x$-10, respectively (Figure 4 (b)). The steric interference from $Ti_3C_2T_x$-X affects the mechanical behavior of composites membrane which is shown in Figure 4 (a) and (b). The Young modulus for pure Nafion membrane was 104.6 MPa which is increased up to 128.4 and 173.7 MPa for Nafion/$Ti_3C_2T_x$-2 and Nafion/$Ti_3C_2T_x$-10, respectively, together with the tensile strength increasing from 16.1 to 18.1 and 24.3 MPa. Same trends were also found for the CS and CS/$Ti_3C_2T_x$-2 and CS/$Ti_3C_2T_x$-10. But elongation reduction behavior was found in membranes due to the presence of inorganic rigid filler.

The $Ti_3C_2T_x$ also improves the water uptake capability of composite membrane. In this context, the pure Nafion membrane showed 21.3% of water uptake with the help of $-SO_3H$ groups which was further increases up to 23.3%, 25.1%, 29.5%, 35.6%, and 37.2% after incorporation of 1%, 2%, 5%, 10%, and 20% $Ti_3C_2T_x$, respectively. The proton conductivity of Nafion and CS membranes are 0.089 and 0.013 S/cm, respectively. The Nafion/$Ti_3C_2T_x$-10 and CS/$Ti_3C_2T_x$-5 composite membranes showed the proton conductivity of 0.161 and 0.069 S/cm with the enhancements of 81% and 431%, respectively. Further, single cell performance of Nafion and Nafion/$Ti_3C_2T_x$-10 at 90 °C under a humidified environment were tested (Figure 4 (e)). The OCV of both cells were found above 0.95 V that indicated no problem of gas crossover occurred. Further, Nafion based cell showed maximum current density and power density of 491.4 mA/cm^2 and 152.6 mW/cm^2, respectively. After incorporation $Ti_3C_2T_x$-10 in Nafion matrix the maximum current density and power density were increases up to 644.0 mA/cm^2 and 193.3 mW/cm^2.

2.2. Anion exchange membrane (AEM)

AEM is a complementary membrane of PEM which contains positively charged groups, such as $-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$, $-NR_3^+$, $-PR_3^+$, $-SR_2^+$, etc., attached to the membrane backbone or polymer and
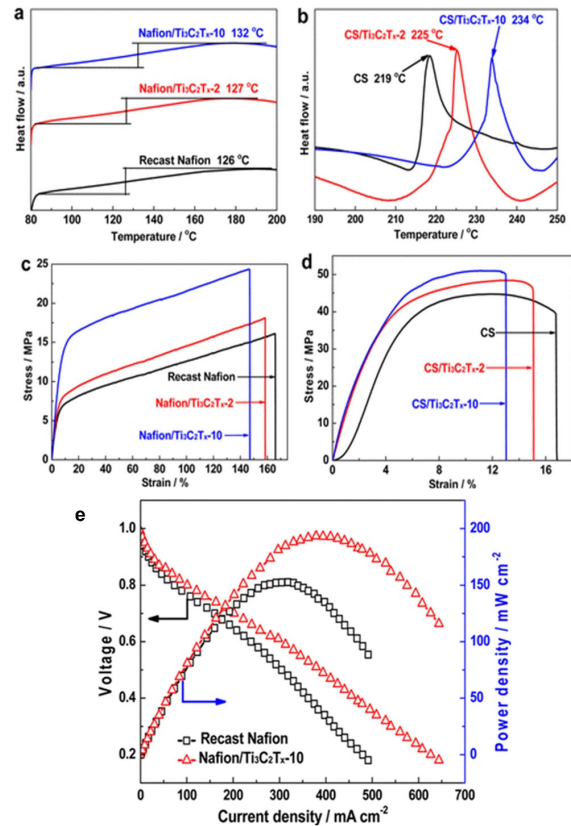

Figure 4. DSC curves of (a) Nafion-based membranes and (b) CS-based membranes. Stress-strain curves of (c) Nafion-based membranes and (d) CS-based membranes, (e) Single H_2/O_2 cell performances of Nafion-based membranes at 90 °C under humidified environment (80% RH) (Reprint with the permission of American Chemical Society)[58].

allow the passage of anions especially -OH⁻ but restrict cations. Recently, AEM based FCs (AEMFCs) are receiving great interest and are the best possible substitute for PEMFCs. AEM has various benefits since it conducts hydroxide (or carbonate) anions during current flow rather than protons. (1) Alkaline settings are significantly easier than acidic ones for the oxygen reduction process (ORR)[59]. This might make it easier to use less expensive non-Pt catalysts with good alkaline environment stability. (2) An alkaline atmosphere improves the electro-oxidation kinetics of a variety of liquid fuels, including unconventional fuels important to the military, like sodium borohydride. (3) More concentrated liquid fuels can be used because the electroosmotic drag brought on by ion transport prevents liquid fuel from crossing over in AEMFCs. The portability of these applications benefits from this. (4) The flexibility in fuel and ORR catalyst selection broadens the parameter space for the identification of highly selective catalysts that are resistant to crossover fuel. The potential benefits of AEMFCs make them an appealing future option.

Presently, various polymer such as polyphenylene oxide (PPO), poly(ether ether ketone) (PEKK), PEEKK, ethylene tetrafluoroethylene (ETFE), polyvinyl alcohol (PVA), polyethyleneimine (BPEI), polytetrafluoroethylene (PTFE), PBI, poly(olefins), styrene, CS, nanofibrillar

cellulose (CNF) and nanocrystalline cellulose (CNC) and many others [60] with various positive charge groups have been used for AEM applications. But these membranes have been suffering from low ionic conductivity, durability chemical and mechanical strength etc.[61] Therefore, recently development for organic-inorganic heterostructure membrane by using various fillers such as graphene, CNTs, metal oxide nanoparticles and MXenes have been gain the attention because they improve the membrane overall properties and performance exceptionally[62]. Among these, recently MXenes have evolved as a very popular filler due to its exceptional properties but in the present scenario, in AEM for FCs application, there are not many reported literatures available till now. Therefore, lots of research needs to be done in this area but some of these are mentioned in this review.

Yang *et al.*[63] prepared two types of MXenes, LiF-$Ti_3C_2T_x$ and NH_4HF_2-$Ti_3C_2T_x$ via selective etching of Ti_3AlC_2 with aqueous solutions of LiF/HCl and NH_4HF_2, respectively. Further, these were used as fillers in quaternized PSU/polyquaternium-10 (QPSU/PQ-10) AEMs with semi-interpenetrating polymer network (SIPN). MXenes improve the ionic conductivity and power density of QPSU/PQ-10. Apart from these, MXenes doping in QPSU/PQ-10 also improves the alkaline stability, oxidation resistance, thermal and mechanical properties along with moderate water uptake and swelling ratio. The 1% of LiF-$Ti_3C_2T_x$ in QPSU/PQ-10 showed the higher IEC of 1.49 meq/g in compared to other percentages (3%, 5%, 7% and 9%). On the other hand, 5% of NH_4HF_2-$Ti_3C_2T_x$ in QPSU/PQ-10 showed a higher IEC of 1.63 meq/g than other percentages. In addition, NH_4HF_2-$Ti_3C_2T_x$ in QPSU/PQ-10 based composites exhibited the highest ionic conductivity and PPD of 88.76 mS/cm at 80 °C and 106.28 mW/cm^2 at 60 °C, respectively, which are 26.3% and 37.5% superior to those of the pure QPSU/PQ-10 AEM.

Zhang *et al.*[64] also incorporated the quaternized MXenes, NH_4HF_2-$Ti_3C_2T_x$ and non-quaternized MXenes, $LiHF_2$-$Ti_3C_2T_x$ in QPSU. The QPSU/NH_4HF_2-$Ti_3C_2T_x$ AEM exhibited 2-folds higher -OH$^-$ conductivity than the pristine QPSU as well as QPSU/$LiHF_2$-$Ti_3C_2T_x$. Also, both MXenes (3 wt%) based AEM increases the PPD up to 74 mW/cm^2 and 101 mW/cm^2 for QPSU/$LiHF_2$-$Ti_3C_2T_x$ and QPSU/NH_4HF_2-$Ti_3C_2T_x$ which were higher than the pure QPSU of 45 mW/cm^2 at 60°C. Also, these AEM exhibited higher mechanical and thermal properties as compared to the pure QPSU membrane. Also, quaternized MXenes helps to improves the ion conductive channels in CS based membrane and greatly enhanced hydroxide ion conductivity, approximately with 172% [65].

3. Conclusion

Charming and potential features of MXenes that make it suitable candidate as filler in PEMs and AEMs that can increase the overall performance of these ion conducting membranes. Based on previous studies, MXenes enhances the proton and hydroxide conductivities with excellent mechanical, chemical and dimensional stabilities which help to increase the overall performance of FCs. At presently, the application of MXenes is very limited for AEMs in comparison to the PEMs,

only few reports are available till date. So, this area could be explored more in the near future to develop high performance FCs. Apart from the utility of the MXenes, presently there are lots of challenges in the synthetic procedures of MXenes synthesis in terms of quality, yield and scalability. Presently, MXenes are generally prepared by using chemical etching. This process has many issues such as use of harsh chemicals and difficulty in controlling the surface functionalities as well as not achieving the complete exfoliation of MAX phase. Therefore, there are many opportunities still remain in MXenes research in terms of development of green synthesis methods as well as excess their potential application in FCs especially as filler for ion exchange membrane in near future.

Acknowledgements

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